

triangles. All previously known salts contain the  $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$  units in arrangements with the  $Fe_3$  triangles parallel or almost parallel throughout the structure. This property is responsible for the pronounced pleochroism of these salts, which strongly absorb blue-green light when the electric vector of the light vibrates parallel to all  $Fe_3$  triangles. In the title compound the pleochroism is weaker, which indicates that the  $Fe_3$  triangles occur in more than one orientation.

I thank Professor Dr A. Preisinger and Dr H. Völlenkle for support and stimulating discussions and Mrs C. L. K. Jelinek for technical assistance. The work was supported by the Fonds zur Förderung der wissenschaftlichen Forschung (project 2178). Calculations were performed at the Interuniversitäres Rechenzentrum Wien with the program systems *MULTAN 74* and *XRAY 72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

*Acta Cryst.* (1980). **B36**, 1288–1291

## The Structure of BaCu and SrCu

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(Received 16 November 1979; accepted 18 January 1980)

### Abstract

BaCu has hexagonal symmetry with  $a = 4.499$  (3),  $c = 16.25$  (1) Å, space group  $P6_3/mmc$ ,  $Z = 4$ ,  $D_x = 4.68$  Mg m<sup>-3</sup>,  $\mu(Mo K\alpha) = 21.5$  mm<sup>-1</sup>. The structure has been solved by trial methods using photographic data, and refined to an  $R$  of 0.090 for 49 observed reflexions. SrCu is isomorphous, with  $a = 4.341$  (3),  $c = 15.38$  (1) Å. The structure of BaCu is formed by a sequence along [001] of slabs of trigonal prisms of Ba centred by Cu atoms and stacked in a close-packing manner. Weak Ba–Ba bonds between adjacent slabs allow BaCu to be considered as a layer compound. A close relationship with the AlB<sub>2</sub> and CrB types is also pointed out.

### Introduction

Amongst the nine possible equiatomic binary compounds between Ca, Sr and Ba on the one hand, and Cu, Ag and Au on the other, seven phases are known

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to exist in the corresponding binary systems; no information is reported in the literature about the existence of the remaining two (BaAg and BaAu). As only CaAg has until now been studied structurally (Calvert, Dunsmore, Kuhl & Tse, 1957), an investigation has been undertaken to elucidate the structure of all these intermetallic compounds. The present work reports the results obtained for the phases SrCu and BaCu, the existence of which was found by Bruzzone (1971) in the study of the respective equilibrium diagrams.

### Experimental

The metals used were barium and strontium from Fluka Co. (Switzerland) of 99.5 wt% purity, and copper from Koch-Light (England) of 99.999 wt% purity. The two compounds were prepared by melting stoichiometric amounts of the component metals in sealed tantalum crucibles. The slowly cooled alloys were well crystallized, with large and very thin plate-like crystals; the

easy cleavage was subsequently recognized as occurring perpendicular to the  $c$  axis of the hexagonal elementary cell. Owing to their high oxidizability, the alloys had to be handled in an inert atmosphere and crushed under paraffin oil; the crystals were sealed in thin glass capillaries under vacuum. The extreme softness of both phases made it difficult to isolate single crystals without introducing plastic deformations, and the X-ray patterns were usually of poor quality. After many trials, two good crystals were found, and the X-ray analysis, carried out by Laue, rotating, Weissenberg and precession methods, confirmed for both compounds the  $6/mmm$  Laue symmetry and the systematic absences ( $hhl$  present only for  $l = 2n$ ) already observed (Bruzzone, 1971). The possible space groups are  $P6_3mc$ ,  $P62c$  and  $P6_3/mmc$ . The lattice constants, obtained from rotation patterns, were  $a = 4.341(3)$ ,  $c = 15.38(1)$  Å for SrCu and  $a = 4.499(3)$ ,  $c = 16.25(1)$  Å for BaCu. The visual comparison of the intensities showed clearly the isomorphism of SrCu and BaCu. A crystal of BaCu with dimensions  $0.18 \times 0.18 \times 0.03$  mm was chosen for the structural determination. The intensities of 183 reflexions, collected on integrated precession photographs, were measured by a microdensitometer and corrected for Lorentz, polarization and absorption effects, the crystal being described as an eight-faced prism. Applying the inter-layer correlation and averaging gave 49 independent reflexions.

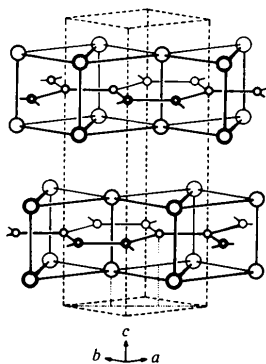


Fig. 1. Perspective view of the BaCu structure: Ba, large circles. The dashed lines outline the elementary cell.

Table 1. Atomic parameters for BaCu with e.s.d.'s in parentheses

Space group  $P6_3/mmc$ . The thermal factor is defined as  $\exp[-8\pi^2 U (\sin \theta/\lambda)^2]$ .

	Equipoint	$x$	$y$	$z$	$U$ (Å <sup>2</sup> )
Ba	$4(f)$	$\frac{1}{3}$	$\frac{2}{3}$	0.1217 (9)	0.028 (4)
Cu(1)	$2(d)$	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	0.038 (12)
Cu(2)	$2(b)$	0	0	$\frac{1}{4}$	0.043 (14)

From a comparison between the cell volume and that calculated using the Ba and Cu elemental atomic volumes, four unit formulae per cell were deduced. A trial structure in space group  $P6_3/mmc$  was proposed on the basis of dimensional considerations and proved to be correct by comparing the experimental and calculated intensities.

Isotropic least-squares refinement was carried out with the *SHELX 76* system of programs (Sheldrick, 1976) over the 49 observed reflexions, which were given unit weights, with atomic scattering factors, corrected for anomalous dispersion, from *International Tables for X-ray Crystallography* (1974). After three cycles convergence was obtained with a conventional  $R$  value of 0.090. Positional and thermal parameters are reported in Table 1.\*

## Discussion

As can be seen in the perspective view of Fig. 1 the structure of BaCu is formed by a sequence along  $[001]$  of slabs of trigonal prisms of Ba centred by Cu atoms and stacked in a close-packing manner. Each slab consists of a  $6^3$  layer of Cu inserted between two close-packed  $3^6$  layers of Ba and the layer-stacking sequence in Pearson's (1972) notation is  $C\bar{c}CBbB$  (Cu underlined). All the copper atoms are then coordinated with six alkaline-earth atoms at the vertices of a trigonal prism and with three copper atoms which emerge from the lateral faces of the prism.

The interatomic distances in BaCu are listed in Table 2, which reports also the distances in SrCu, assuming for this compound the same value of the atomic parameter found for BaCu. The Ba—Cu distances show a 6% contraction as regards the sum of the metallic radii, and the Cu—Cu distance (2.60 Å) is only slightly larger than the metallic diameter of copper (2.56 Å). The Ba—Ba distances, which correspond to the height and the base of the prisms (4.17 and 4.50 Å, respectively), are shorter than or equal to the metallic diameter of barium (4.50 Å). In contrast, the Ba—Ba distance between two contiguous Ba layers (4.73 Å) is clearly larger than the Ba metallic diameter, and is probably indicative of a weak bond. As this distance is the only connexion between contiguous slabs of prisms, BaCu may be considered a layer compound in the chemical sense and its properties like easy cleavage and high softness can be justified. The same large value of the Ba—Ba distance is found also in  $Ba_2Cd$  and  $Ba_2Hg$  ( $MoSi_2$  type), which show features of layer compounds (Merlo, 1976).

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35105 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances (Å) in BaCu and SrCu*

The e.s.d.'s of BaCu are less than 0.02 Å.

BaCu		SrCu	
Ba—1Ba	4.17	Sr—1Sr	3.95
—6Ba	4.50	—6Sr	4.34
—3Ba	4.73	—3Sr	4.51
—3Cu(1)	3.33	—3Cu(1)	3.19
—3Cu(2)	3.33	—3Cu(2)	3.19
Cu(1)—6Ba	3.33	Cu(1)—6Sr	3.19
—3Cu(2)	2.60	—3Cu(2)	2.51
Cu(2)—6Ba	3.33	Cu(2)—6Sr	3.19
—3Cu(1)	2.60	—3Cu(1)	2.51

The structure of BaCu can be related to those of other layer phases which present the same stacking of trigonal-prism slabs. A very similar atomic arrangement occurs in  $\delta_{H}^{IV}\text{-W}_{0.6}\text{N}$ , studied by electron diffraction on thin films (Khitrova & Pinsker, 1962), where weak W—W bonds connect the prism slabs. Moreover, BaCu can be considered as a filled structure of the high-temperature form of  $\text{NbS}_2$  (stacking sequence  $\underline{BABCAC}$ ; Nb underlined), and of  $\beta\text{-MoS}_2$  (sequence  $\underline{CBCBCB}$ ; Mo underlined), discussed by Pearson (1972). In these last two compounds only half of the prisms formed by sulphur are centred by the metal atoms and the slabs are held together by S—S van der Waals bonds.

Amongst the 43 hitherto known equiatomic intermediate phases formed by the alkaline earths with all of the other elements (save nitrogen, phosphorus, chalcogens and halogens), only 33 were structurally determined. Most compounds crystallize in the CrB structure type (SrPd, BaPd, CaAg, CaGa, CaSi, SrSi, BaSi, CaGe, SrGe, BaGe, CaSn, SrSn, BaSn, SrPb and BaPb) and in the CsCl type (CaPd, BaZn, CaCd, SrCd, BaCd, CaHg, SrHg, BaHg, CaIn, CaTl and SrTl). The remaining ones belong to the BaCu type (SrCu and BaCu), to the SrAl type (SrAl and SrGa), to the  $\text{Na}_2\text{O}_2$  type (CaAs and SrAs) and to the AuCu type (CaPb). As the BaCu and the CrB types are both based on the trigonal prismatic coordination, some correlation between these structures may be expected. Moreover, the trigonal prism linkage coefficient, defined by Parthé & Moreau (1977) as the average number of centred prisms which share the atoms forming the prisms, is 6 for BaCu, as in the CrB structure.

On the other hand, several mechanisms of geometrical derivation of the CrB structure from the  $\text{AlB}_2$  type have been described (Pearson, 1972; Hulliger, 1976). The BaCu structure can be also derived from that of  $\text{AlB}_2$  in a similar way. In Fig. 2 the structures of  $\text{BaAu}_2$  ( $\text{AlB}_2$  type; Bruzzone, 1970), BaCu and CaAg (CrB type; Calvert, Dunsmore, Kuhl & Tse, 1957; Schob & Parthé, 1965) are drawn. The ratio of height to base of

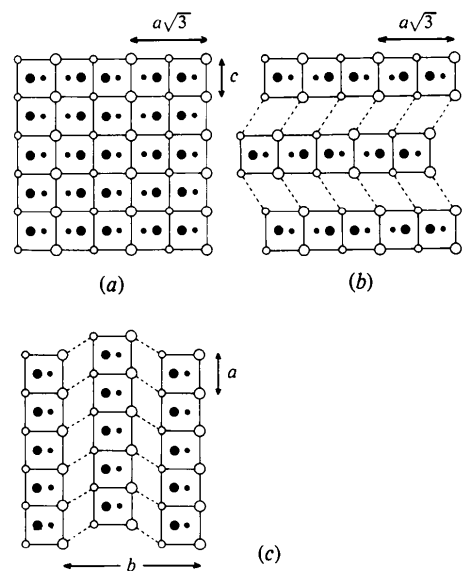


Fig. 2. The geometrical relationships among the  $\text{AlB}_2$ , BaCu and CrB structure types. (a)  $\text{BaAu}_2$ ,  $\text{AlB}_2$  type; (b) BaCu; (c) CaAg, CrB type. The open circles correspond to alkaline-earth elements, the filled circles to Au or Cu or Ag atoms. The larger circles are in the plane of the page, the smaller ones are below and above the plane of the page.

the trigonal prisms is nearly the same for the three compounds, namely 0.87. As can be seen in the figure, the BaCu structure is obtained from the  $\text{AlB}_2$  type (stacking sequence  $\underline{Aa}$ ; Al underlined) by removing alternate boron networks and shifting alternate slabs of trigonal prisms along the  $[\bar{1}10]$  direction by  $a/\sqrt{3}$ . The CrB structure is also obtained from the  $\text{AlB}_2$  type by removing alternate aligned chains of boron atoms and shifting alternate columns of prisms along  $[001]$  by  $c/2$ . While in BaCu the copper atoms again form a network, like boron in  $\text{AlB}_2$ , in the CrB-type compounds the atoms at the centre of the prisms form infinite chains. Moreover, no layer-compound feature occurs in the CrB type, the blocks of prisms being connected to each other by normal bonds.

We wish to thank Professor A. Iandelli for his interest in this work, and the Consiglio Nazionale delle Ricerche for financial support.

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*Acta Cryst.* (1980). **B36**, 1291–1294

## Etude Structurale des Oxysulfures de Chrome(III) et de Terres Rares.

### I. Structure de l'Oxysulfure LaCrOS<sub>2</sub>

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(Reçu le 10 juillet 1979, accepté le 21 janvier 1980)

#### Abstract

LaCrOS<sub>2</sub> is orthorhombic, space group *Pbnm*, with unit-cell constants  $a = 11.193$  (6),  $b = 8.398$  (2),  $c = 3.704$  (3) Å,  $Z = 4$ ,  $D_m = 5.2$  (1),  $D_x = 5.16$  Mg m<sup>-3</sup>. The crystal structure has been solved from four-circle diffractometer data by Patterson and Fourier syntheses, and refined by the least-squares method to a final *R* value of 0.024 for 961 observed structure factors. The La is nine-coordinated in tricapped trigonal prisms containing three O and six S atoms; the Cr is six-coordinated in octahedra formed by one O and five S atoms. The structure has a three-dimensional arrangement and can be regarded as being built up from layers of [LaO<sub>3</sub>S<sub>6</sub>] polyhedra alternating with layers of [CrOS<sub>5</sub>] octahedra. In the [CrOS<sub>5</sub>] layers, two octahedra are bonded sharing an S–S edge.

#### Introduction

Dans une note antérieure (Vovan, Dugué & Guittard, 1978) nous avons relaté l'existence d'une famille d'oxysulfures mixtes de formule générale *L*CrOS<sub>2</sub> (*L* = La à Sm). Ces composés appartiennent à deux types cristallins différents: l'un est propre au lanthane, l'autre ne s'observe qu'avec les autres lanthanides, du cérium au samarium. Dans le présent article nous décrivons la structure cristalline de l'oxysulfure LaCrOS<sub>2</sub>.

#### Préparation

Nous préparons cet oxysulfure à partir d'un mélange d'oxyde La<sub>2</sub>O<sub>3</sub> et des sulfures La<sub>2</sub>S<sub>3</sub> et Cr<sub>2</sub>S<sub>3</sub>, en

proportion correspondant à la formule LaCrOS<sub>2</sub>, chauffé pendant une journée à 1223 K en ampoule de silice vidée d'air et scellée, puis recuit vers 1000 K pendant une semaine.

Des monocristaux ont été obtenus en chauffant la poudre cristalline avec du bromure de potassium, toujours en ampoule de silice, à la température de 1123 K pendant un mois. Après lavage à l'eau froide on recueille des cristaux dont le diagramme de Debye et Scherrer est identique à celui de la poudre initiale.

#### Données cristallographiques

Ces cristaux se présentent sous la forme de petites plaquettes transparentes, de couleur rouge sombre, allongées suivant la direction [001]. Les clichés d'oscillation et de Weissenberg révèlent une symétrie orthorhombique; les valeurs des paramètres du réseau ont été affinées par la méthode des moindres carrés sur 24 réflexions intenses mesurées à l'aide d'un diffractomètre.

Les extinctions systématiques sont caractéristiques des deux groupes spatiaux *Pbnm* et *Pbn2<sub>1</sub>*, permutations respectives des groupes *Pnma* et *Pna2<sub>1</sub>* de *International Tables for X-ray Crystallography* (1969).

#### Détermination de la structure

Nous avons choisi un cristal de forme sensiblement aciculaire (30 × 35 × 200 μm) pour réduire les effets de l'absorption ( $\mu = 16$  mm<sup>-1</sup> pour la radiation Mo K $\alpha$ ).

Les intensités de 1304 réflexions indépendantes sont enregistrées à l'aide d'un diffractomètre automatique à © 1980 International Union of Crystallography